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Preparation and kinetic analysis of Li_4SiO_4 sorbents with different silicon sources for high temperature CO_2 capture

SHAN ShaoYun, JIA QingMing, JIANG LiHong, LI QinChao, WANG YaMing & PENG JinHui*

Kunming University of Science and Technology, Kunming 650093, China

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Using diatomite and analytical pure SiO_2 as silicon sources, Li_4SiO_4 sorbents for high temperature CO_2 capture were prepared through solid-state reaction method. Phase composition was analyzed by X-ray diffraction, and the CO_2 absorption capacity and absorptoin-desorption performance were studied by the simultaneous thermal thermogravimetric analyzer (TG-DSC). The results showed that silicon source had an important influence on CO_2 absorption properties. The kinetic parameters for the chemisorption and diffusion processes were obtained by the isothermal study for different silicon sources. The results showed that the activation energies for these two processes were estimated to be 105.427 and 35.928 kJ/mol for the sample with analytical pure SiO_2 (AS). While for the sample with diatomite (DS), the activation energies for these two processes were estimated to be 78.500 and 20.439 kJ/mol, respectively.

kinetic, silicon sources, lithium silicate, CO_2 capture

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The increasing CO_2 concentration in the atmosphere due to fossil fuel burning has been considered as a major contributor to the global warming. So the separation, recovery and storage/utilization of CO_2 have attracted considerable attention in recent years. CO_2 can be removed from flue gas and waste gas streams by various methods such as membrane separation, wet absorption, and dry absorption [1–4]. However, these methods need to consume a lot of energy. Hence, the materials with high CO_2 capture capacity at high temperature are desirable.

In recent years, the development of regenerable sorbents for high temperature CO_2 capture has received increasing attention [5–7]. Compared with other sorbents, Li_4SiO_4 has the better CO_2 absorption properties over a wide range of temperature and CO_2 concentration [8,9]. In order to study the absorption mechanism of Li_4SiO_4 materials, some researchers made some kinetic study about Li_4SiO_4 materials [10]. However, kinetic study about different silicon sources has not been reported.

In this paper, we firstly developed novel low-cost Li_4SiO_4 sorbents for high temperature CO_2 capture using diatomite as silicon source. The effect of different silicon sources on the absorption capacity was investigated by studying their kinetic characteristics. In the following paper, DS and AS stand for diatomite and analytical pure SiO_2, respectively.

1 Experimental

Diatomite (75%SiO_2, C.R., Shanghai Fengxian Reagent Co. Ltd., China) and SiO_2 (99%, A.R., Traditional China Medicine Chemical Reagent Co. Ltd., China) were used as silicon sources. The properties for diatomite are shown in Table 1. Li_2CO_3 (97%, A.R., Tianjin Fengchuan Chemical Reagent Co. Ltd., China) was used as the starting powders. Li_4SiO_4 materials were synthesized according to reaction (1) at 700°C for 2 h.

*Corresponding author (email: Jhpeng@kmust.edu.cn)

Table 1 Diatomite composition analysis

Compostion	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	Loss	Others
Content (wt%)	75.26	14.33	2.31	1.02	1.56	4.35	1.17

$$2Li_2CO_3 + SiO_2 = Li_4SiO_4 + 2CO_2 \quad (1)$$

Crystalline phases were identified by XRD (D8ADVANCE, Germany) analysis. The absorption properties of Li_4SiO_4 materials with different silicon sources were investigated into the gas mixture (50 mL/min N_2 and 50 mL/min CO_2) by TG-DSC (STA 449 F3, Netch Co. Ltd., Germany). The absorption reaction is

$$Li_4SiO_4 + CO_2 = Li_2SiO_3 + Li_2CO_3 \quad (2)$$

As seen from reaction (2), the theoretical absorption capacity of Li_4SiO_4 is 36.7 wt%.

2 Results and discussion

2.1 Phase composition and microstructure of Li_4SiO_4 sorbents

Figure 1 shows the diffractograms of Li_4SiO_4 sorbents with different silicon sources prepared at 700°C for 2 h. As shown in Figure 1, Li_4SiO_4 phase with a=5.30 Å, b=6.32 Å, c=5.45 Å (JCPDS: 24-0650) was the main phase for the sample with DS and AS, which indicated that the reaction had happened completely according to reaction (1). While a small quantity of $LiAlSi_2O_6$ phase (JCPDS: 33-0786) was observed for the sample with DS. The occurrence of $LiAlSi_2O_6$ phase was resulted from the reaction between Al_2O_3 phase coming from diatomite and Li_2CO_3. Different lithium aluminates have different absorption properties for CO_2. $LiAlO_2$ did not seem to have good absorption properties for CO_2, and Li_5AlO_4 showed excellent behavior as a possible CO_2 captor [11]. However, the absorption properties of $LiAlSi_2O_6$ for CO_2 are not known.

Figure 2 shows the microstructure of diatomite and the Li_4SiO_4 sorbents with DS and AS. Seen from Figure 2(a), diatomite had rich pore structure and uniform pore distribution with the pore size of 0.5–1.0 μm. Seen from Figure 2(c), the sample with AS was mainly composed of some small spherical particles and a portion of large polygonal particles. Figure 2(b) shows that the sample with DS showed more uniform microstructure, which was mainly composed of homogenuous spherical particles with a particle size of about 1–3 μm. Obviously, the microstructure of the Li_4SiO_4 with DS did not inherit that of diatomite, but the structure of silicon source had an important influece on the microstructure of the final Li_4SiO_4 sorbents. The specific surface areas for the sample with DS and AS under the same preparation condition are 1.75 and 1.15 m^2/g, respectively.

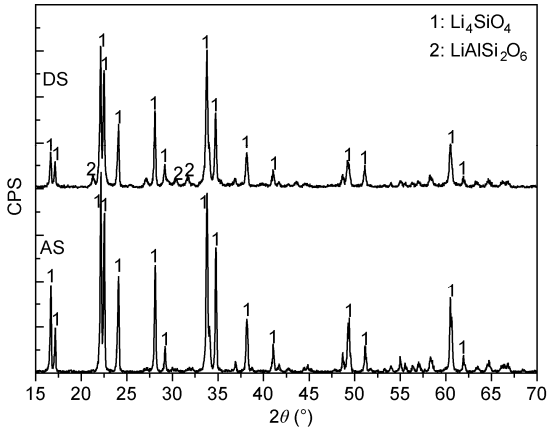

Figure 1 XRD patterns of Li_4SiO_4 sorbents with different silicon sources.

2.2 Effect of different silicon sources on absorption properties

Figure 3 shows the effect of different silicon sources on absorption capacity. As shown in Figure 3, the sample with DS had higher absorption capacity than that with AS at the same retaining time. The sample with DS had much quicker absorption rate before 10 min, and the absorption capacity of the sample with DS was almost twice as high as that of the sample with AS at 10 min. In addition, the absorption reaction reached equilibrium at 80 min for the sample with DS, but the sample with AS did not still reach equilibrium until 200 min. The maximum absorption capacity (28.62 wt%) for the sample with DS, being 78% of the theoretical absorption capacity, was higher than that (22.08 wt%) for

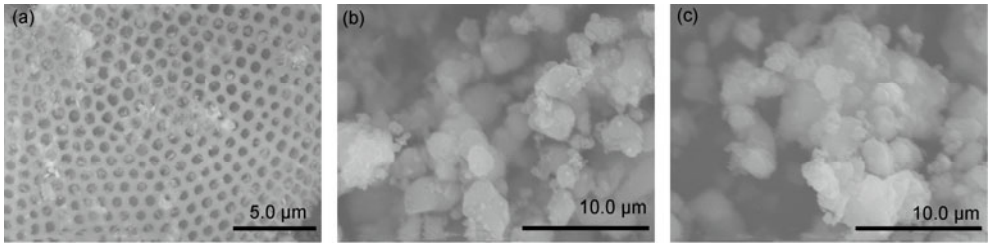

Figure 2 SEM images of diatomite (a), the Li_4SiO_4 sorbents with DS (b) and AS (c).

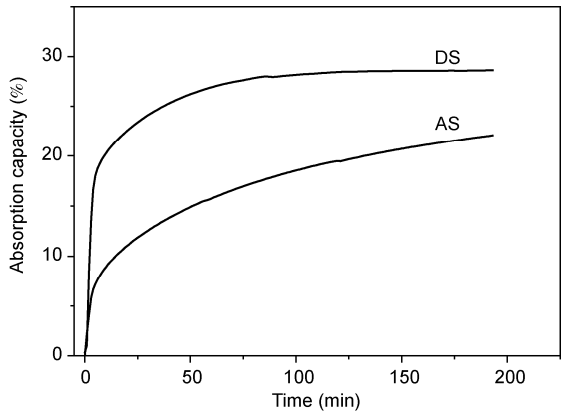

Figure 3 Isotherms of Li_4SiO_4 materials with different silicon sources at 620°C.

the sample with AS, which probably resulted from the larger specific surface area and more uniform microstructure for the sample with DS. Besides this, the results were also explained by the following kinetic analysis.

2.3 Kinetic analysis for Li_4SiO_4 sorbents with different silicon sources

Figure 4 shows the isothermal graphs of Li_4SiO_4 materials with AS at different temperatures. As shown in Figure 4, the absorption capacity and the absorption rate increased with the absorption temperature. At 550°C or 600°C, Li_4SiO_4 materials only absorbed a small quantity of CO_2 (about 10 wt%) at 200 min, while the CO_2 absorption capactity reached 22.11 wt% at 620°C at 200 min.

In order to obtain some kinetic information about the CO_2 absorption, some isothermal analyses were performed at different temperatures into the mixture gas (50 mL/min N_2 and 50 mL/min CO_2) (Figure 4). Seen from Figure 4, three absorption curves presented simlilar behaviors, and the data was fitted according to a double exponential model: $y=A\exp(-k_1x)+B\exp(-k_2x)+C$, where y represents absorption capacity, x is absorption time, k_1 and k_2 are the exponential constants, and A, B, and C are the pre-exponential factors. The kinetic parameters obtained at three temperatures are shown in Table 2. As can be seen, k_1 (chemisorption) values are about 10 times higher than those of k_2 (diffusion), indicating that the diffusion is the limiting step of the total reaction. For a model of these characteristics, the gradients of these best fit lines usually confirm to the Arrhenius equation, so that

$$k = k_0 \exp\left(-\frac{E}{R_g T}\right),$$

where k is the reaction rate constant, k_0 is the pre-exponential factor, E is the activation energy, R_g is the gas constant, and T is absolute temperature. Figure 5 shows the plots of ln$k$ versus 1/T. The curves obviously show a linear trend for

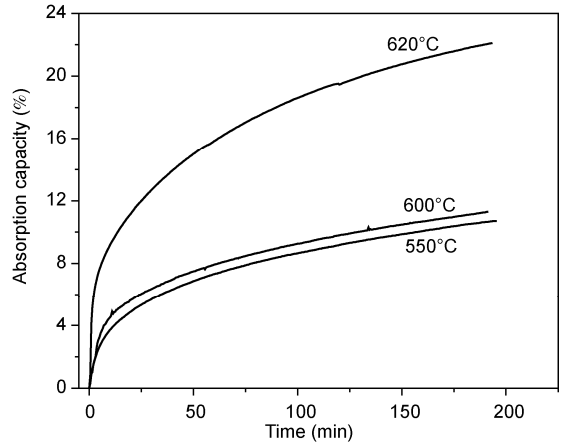

Figure 4 Isotherms of Li_4SiO_4 materials with AS.

Table 2 Kinetic parameters obtained from the experimental data fitted to a double exponential model for the sample with AS

T (°C)	k_1 (1/s)	k_2 (1/s)	R
550	0.08905	0.00727	0.99964
600	0.25336	0.00899	0.99869
620	0.28016	0.01134	0.99855

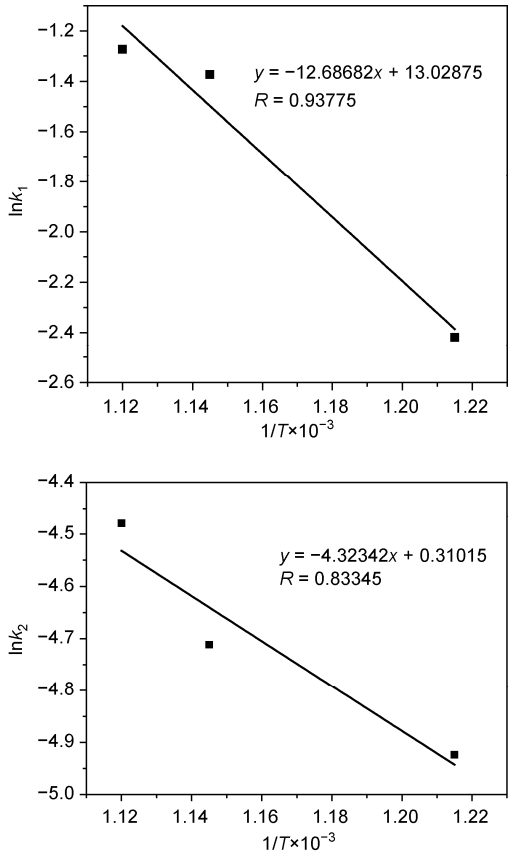

Figure 5 Plots of ln$k$ versus 1/T for chemisorption (k_1) and diffusion (k_2) on Li_4SiO_4 with AS.

both chemisorption process and diffusion process. Hence, the activation energies for the chemisorption and diffusion processes were estimated to be 105.427 and 35.928 kJ/mol, respectively. As can be seen, the activation energy of the chemisorption process is almost three times as high as that of the diffusion process, which showed that the chemisorption process was more dependent on the temperature.

In order to analyze the effect of silicon source on the kinetic reaction, the Li_4SiO_4 with DS was studied under the same conditions. Figure 6 shows the isothermal graphs of this sample at three temperatures. The curves behavior was similar to the results in Figure 4. It was obviously seen from Figure 6 that the maximum absorption capacity (28.64 wt%) was much higher than that (11.33 wt%) of the Li_4SiO_4 with AS at 600°C at 200 min. In order to analyze this reason, the experimental data were also fitted to the double exponential model, the results are shown on Table 3. As shown in Table 3, the ratio of k_1 and k_2 is more than 15, indicating that diffusion is also the limiting step. Following the same procedure, these data were fitted according to the Arrhenius theory (Figure 7). It is found that the results were better than those of the first data. The activation energies for chemisorption process and diffusion process were estimated to be 78.500 and 20.439 kJ/mol, respectively. By comparing the activation energies of two different silicon sources, some significant results were obtained. Obviously, the activation energies of the chemisorption process and diffusion for the sample with AS were higher than those of the sample with DS, indicating that the sample with DS had the higher reactivity and the better diffusivity due to structural differences

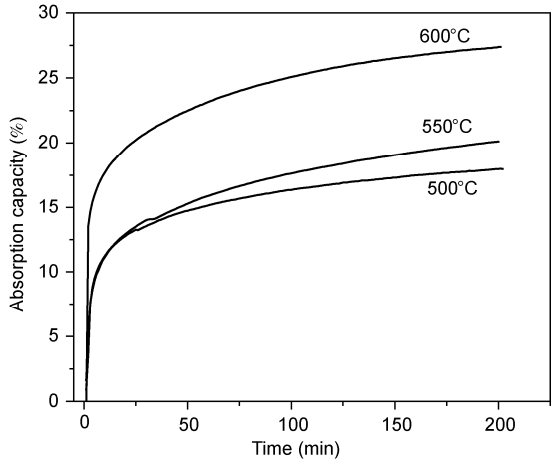

Figure 6 Isotherms of Li_4SiO_4 materials with DS.

Table 3 Kinetic parameters obtained from the experimental data fitted to a double exponential model for the sample with DS

T (°C)	k_1 (1/s)	k_2 (1/s)	R
500	0.16376	0.01122	0.99937
550	0.31428	0.01059	0.99817
600	0.35881	0.01331	0.99516

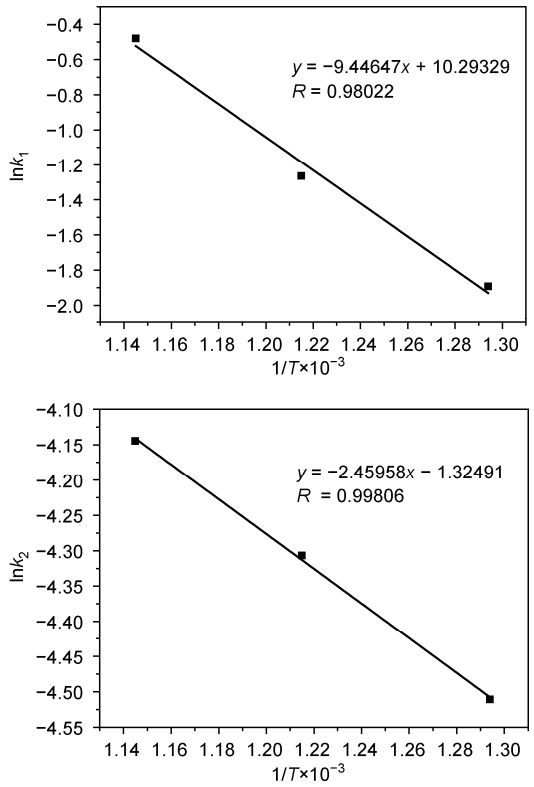

Figure 7 Plots of ln$k$ versus 1/T for chemisorption (k_1) and diffusion (k_2) on Li_4SiO_4 with DS.

produced by the aluminum and other elements present on the diatomite [8,12]. The k_1/k_2 ratio of the sample with DS was lower than that of the sample with AS, which showed the diffusion rate was relative quicker for the sample with DS. Seen from the above kinetic analysis for different silicon sources, Li_4SiO_4 sorbents with AS and DS for CO_2 absorption followed a double absorption mechanism [13].

2.4 Absorption-desorption performance measurement for DS

In order to investigate the cyclic absorption properties of the sample with DS, the absorption-desorption test was carried out at a fixed temperature (700°C) in a Netzsch thermogravimetric analyzer. During the test, a mixture gas (50 mL/min N_2 and 50 mL/min CO_2 for absorption and 100 mL/min N_2 for desorption) were introduced into the system every 30 min. Figure 8 shows the absorption-desorption cycle number of Li_4SiO_4 sorbents with DS. As shown in Figure 8, with increasing cycle number, the absorption capacity decreased 2.35 wt% from the first cycle (34.62 wt%) to the 10th cycle (32.27 wt%). This is probably beacause Li_4SiO_4 sorbents with DS have particular structure, which refrained Li_4SiO_4 sorbents from sintering in multinumber cycles. Compared with the lithium-based sorbents prepared by Marin et al. [14], the resultant Li_4SiO_4 sorbents have the higher CO_2 absorption capacity and better cyclic properties.

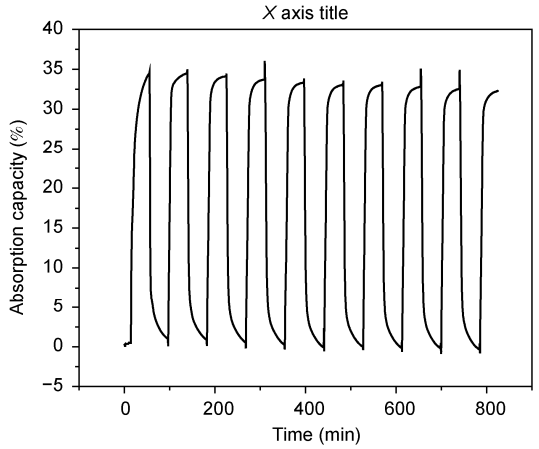

Figure 8 Absorption-desorption performance of the Li_4SiO_4 with DS.

Therefore, the resultant Li_4SiO_4 sorbents with DS should have a potential application prospect for high temperature CO_2 capture.

3 Conclusions

Novel Li_4SiO_4 sorbents from diatomite for high temperature CO_2 capture were prepared at low preparation cost. Effect of different silicon sources on CO_2 absorption capacity was investigated by analyzing the kinetic characteristics. The following conclusions were obtained:

(1) The sample with DS had higher absorption capacity and absorption rate than that with AS at the same retaining time. The maximum absorption capacity of the sample with DS reached 28.62 wt%, being 78% of the theoretical absorption capacity.

(2) Some kinetic information about the CO_2 absorption was obtained according to the doube exponential model and the Arrhenius equation. The lower activation energies of the sample with DS for the chemisorption process and diffusion process were resulted from structural differences produced by the aluminum and other elements present on the diatomite.

(3) The Li_4SiO_4 with DS had a good absorption-desorption performance. The absorption capacity only decreased 2.35 wt% from the first cycle (34.62 wt%) to the 10th cycle (32.27 wt%).

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